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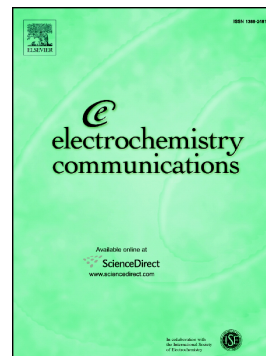
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**Temperature effect upon the thermoelectrochemical
potential generated between lithium metal and lithium ion
intercalation electrodes in symmetric and asymmetric
battery arrangements**

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Abstract

The evaluation of batteries under thermal gradients is essential for safety and longevity reasons, and to investigate power generation via the thermogalvanic effect. The thermogalvanic Seebeck coefficient of lithium metal ($+1.0 \text{ mV}\cdot\text{K}^{-1}$) and solid lithium ferri/ferrocyanide intercalation electrodes ($-0.6 \text{ mV}\cdot\text{K}^{-1}$) were determined. The measured Seebeck coefficients of identical asymmetric cells containing both electrodes deviated from the expected values, having Seebeck coefficients which also varied as a function of thermal conditions ($+0.7$ to $+4.3 \text{ mV}\cdot\text{K}^{-1}$). This work demonstrates that the thermal responses of asymmetric battery assemblies are more complex than predicted based upon their individual half-cell performances in symmetric cells.

Keywords:

Seebeck coefficient; thermal energy; temperature effect on battery; thermocell; thermogalvanic

1 Introduction

Batteries have revolutionised modern society but increased usage has been accompanied with increased risk of malfunction; as high enthalpy chemical devices, thermal runaway (leading to a fire) occurs when assembly or management is poor [1]. As ever-larger battery stacks become prevalent, thermal management becomes more crucial, as does understanding any 'thermoelectrochemistry' due to temperature gradients/vari-ations.

While elevated temperatures can lead to fires [1], even minor temperature variations can lead to significant decreases in the performance of lithium ion batteries [2].

The potential of the $\text{Li}_{(\text{s})} \rightarrow \text{Li}^+_{(\text{solvated})} + \text{e}^-$ process exhibits a significant temperature dependence; it is primarily driven by the entropy of (de)solvation [3]. Various values have been reported: $+0.86 \text{ mV}\cdot\text{K}^{-1}$ (cyclic voltammetry; 8 mM $\text{Li}[\text{PF}_6]$ in THF, relative to ferrocene|ferrocenium) [4], $+1.3 \text{ mV}\cdot\text{K}^{-1}$ (non-isothermal potential measurements; 1 M $\text{Li}[\text{NTf}_2]$ in tetraglyme) [5] and $+1.6 \text{ mV}\cdot\text{K}^{-1}$ (electrochemical microcalorimetry; 1 M $\text{Li}[\text{PF}_6]$ in 1:1 ethylene carbonate:dimethyl carbonate) [3]. Such systems have also been shown to form thermogalvanic cells, where a temperature difference across the cell generated an electrical current [5]. These values are temperature coefficients of the electrode potential (thermogalvanic Seebeck coefficients) and are distinct from the thermoelectric Seebeck coefficient (lithium metal; $+0.015 \text{ mV}\cdot\text{K}^{-1}$ [6-8]). The former are electrochemical phenomena relating to redox and solvation processes, whereas the latter is a phenomenon of electron conductors and semi-conductors.

Hudak and Amatucci investigated the temperature dependence of two lithium ion intercalation materials [9]. Seebeck coefficients of *ca.* $+0.6 - +1.2 \text{ mV}\cdot\text{K}^{-1}$ were observed; the value was largely independent of the electrode material used but was dependent upon the extent of lithium intercalation [9]. Notably, they also formed a thermogalvanic cell, and electrical current could be generated by a temperature difference.

Recently, Magnusson *et al.* investigated the temperature dependence of an asymmetric cell, where one electrode was lithium metal, and the other a lithium intercalation compound [10]. Heating the electrodes equally, the potential difference was referred to the Seebeck coefficient, and values between -0.8 and $+1 \text{ mV}\cdot\text{K}^{-1}$ were observed (dependent on the degree of intercalation) [10]. Crucially, the authors assumed the Seebeck coefficient of lithium metal was $0 \text{ mV}\cdot\text{K}^{-1}$ [10], presumably because they muddled thermoelectric ($+0.015 \text{ mV}\cdot\text{K}^{-1}$ [6-8]) and thermogalvanic (up to $+1.6 \text{ mV}\cdot\text{K}^{-1}$ [3]) Seebeck coefficients. Interpretation of these observations focussed upon possible solid-state (thermoelectric) attributes of the intercalation compound, without considering the role of lithium ion intercalation/solvation. The sign and magnitude of these Seebeck coefficients for the lithium intercalation compounds [10] also deviate significantly from thermogalvanic values observed for lithium metal [3-5] and other lithium intercalation electrodes [9] in contact with a lithium-ion-containing electrolyte.

Given the relevance of temperature-dependent studies to battery longevity and safety [1], to thermogalvanic waste heat harvesting [5, 9] – and the discrepancy in the literature [9, 10] – a detailed investigation of lithium metal cells, lithium intercalation compound cells, and asymmetric cells was performed, under different thermal conditions.

2 Materials and methods

Solid $\text{Li}_{3.5}\text{Fe}(\text{CN})_6$ composite electrodes were prepared through grinding 70 wt% lithium ferricyanide and lithium ferrocyanide (1:1) with 20 wt% polyvinylidene difluoride and 10 wt% carbon black to give a visually uniform fine powder which was mixed with *N*-

methylpyrrolidone to give a homogenous slurry. This slurry was cast onto copper foil and dried in a vacuum oven (18 h, 110 °C) then cut into discs.

Cells were prepared as previously reported [5] using 1 M lithium perchlorate (LiClO_4) in 1:1 diethyl carbonate (DEC):ethylene carbonate (EC) as the electrolyte. The $\text{Li}_{3.5}\text{Fe}(\text{CN})_6$ was insoluble in this medium.

Symmetric cells were prepared with either solid lithium (Figure 1d) or composite $\text{Li}_{3.5}\text{Fe}(\text{CN})_6$ (Figure 1e) electrodes. Asymmetric cells (Figure 1f) were prepared with one solid lithium electrode and one composite $\text{Li}_{3.5}\text{Fe}(\text{CN})_6$ electrode.

Variable temperature measurements of symmetric lithium cells were performed using our previously reported apparatus [11-13], using a 'stepped gradient' (Figure 1a). The cold side was kept at 20 °C while the hot side had the temperature varied in 10 °C increments from 20 °C to 70 °C then back down to 20 °C. Each step lasted 1000 s. The open circuit potential was averaged over the last 500 s of each step. The datum reported is the average of at least triplicate measurements; the uncertainty reported is the standard deviation of these measurements.

Two forms of pulsed thermal measurements were also used. A 'pulsed gradient' profile akin to the method reported by Hudak and Amatucci [9] was used (Figure 1b). One side was kept at 20 °C while the other was pulsed in 1 °C increments (21 °C to 25 °C; then back to 21 °C, returning to 20 °C between each pulse; each segment lasted for 600 s). To compensate for the drifting background potential the 20 °C regions were fitted to a three-phase decaying exponential. The potential at each temperature was calculated using the average of the last 300 s of the background subtracted potential. Data reported are the average of three

measurements of three cells (*i.e.* nine measurements per value), the uncertainty reported is the standard deviation of the nine measurements.

A ‘pulsed isothermal’ profile akin to that reported by Magnusson *et al.* [10] was also used (Figure 1c). This mirrored the ‘pulsed gradient’ measurement except that both sides were heated equally (*i.e.* remained isothermal).

For the asymmetric cells, the potential and the temperature dependence of the cell potential are reported for the $\text{Li}_{3.5}\text{Fe}(\text{CN})_6$ electrode relative to the lithium metal electrode.

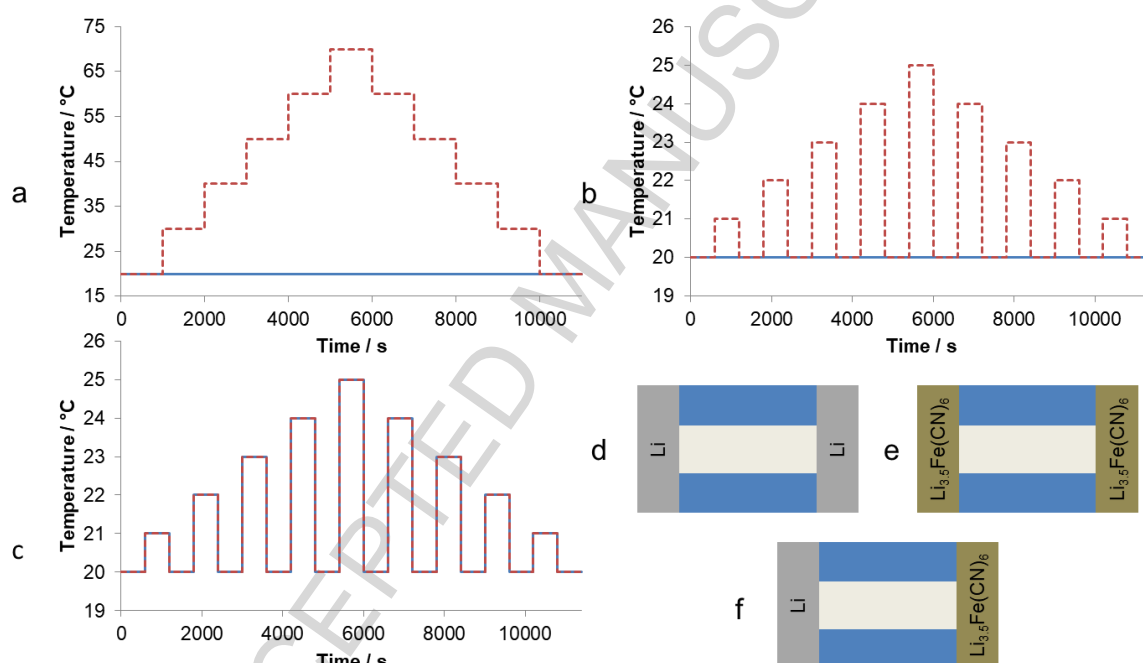


Figure 1 - Stepped gradient (a), pulsed gradient (b) and pulsed isothermal (c) temperature profiles used. Red and blue represents the temperature of each side of the cells. Schematic of the different cells tested showing the symmetric lithium cell (d), the symmetric lithium ferri/ferrocyanide cell (e) and the asymmetric cell (f).

3 Results and Discussion

In a lithium metal cell (*cf.* Figure 1d) the Seebeck coefficient was measured for two lithium metal electrodes in contact with the common battery electrolyte 1 M LiClO_4 in 1:1 DEC:EC. A stepped temperature gradient was applied across the symmetrical lithium metal cell (*cf.* Figure 1a), with the temperature of one electrode varied from 20 to 70 °C. The resulting

potential difference mirrored the applied temperature difference (Figure 2a); this represents the temperature dependence of the process $\text{Li}_{(s)} \rightarrow \text{Li}^+_{(\text{solvated})} + e^-$. It displayed no hysteresis, with excellent linearity in the plot of E vs ΔT – the gradient yielded a temperature dependence of $+0.98 \pm 0.03 \text{ mV}\cdot\text{K}^{-1}$. Notably, this value falls within the range of values for $\text{Li}_{(s)} \rightarrow \text{Li}^+_{(\text{solvated})} + e^-$ in non-aqueous solvents ($+0.9$ to $+1.6 \text{ mV}\cdot\text{K}^{-1}$ [3-5]).

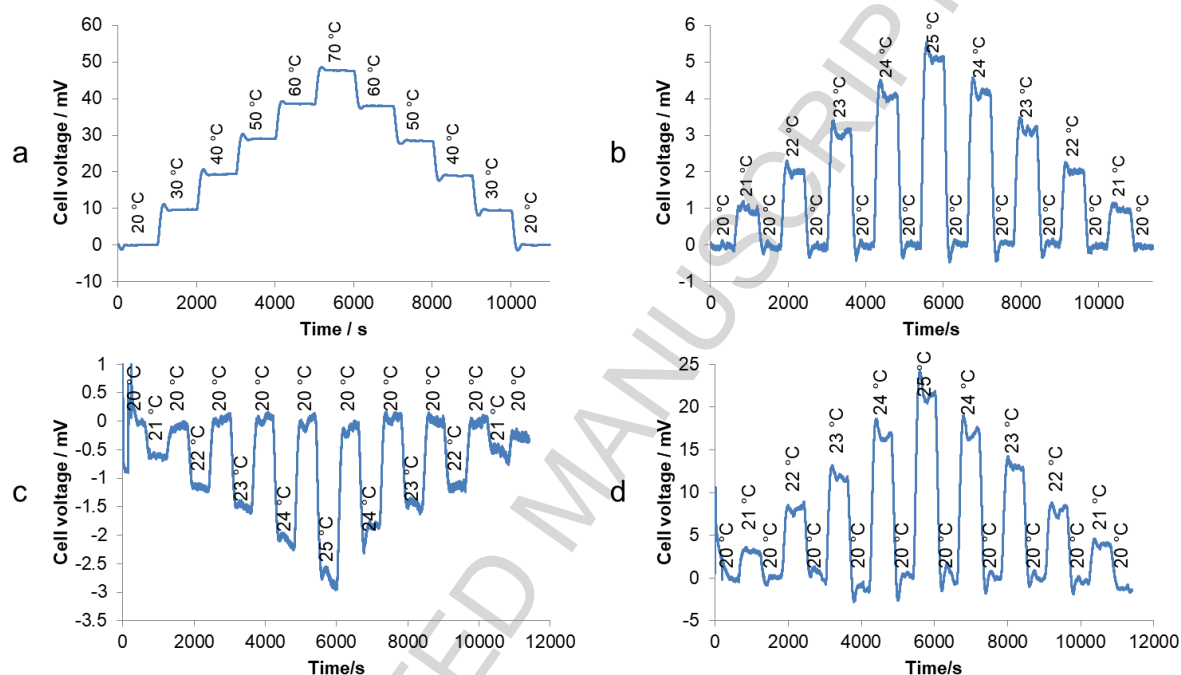


Figure 2 - Open circuit potential measurements with temperature overlaid for a stepped gradient measurement of a cell with lithium electrodes (a), pulsed gradient measurements of cells with lithium electrodes (b) and $\text{Li}_{3.5}\text{Fe}(\text{CN})_6$ electrodes (c) and a pulsed isothermal measurement of a cell containing lithium and $\text{Li}_{3.5}\text{Fe}(\text{CN})_6$ electrodes.

A ‘pulsed gradient’ heating profile measurement (Figure 1b) of symmetrical lithium metal cells gave the same value (Table 1). A ‘pulsed isothermal’ measurement (Figure 1c) of the cell gave a Seebeck coefficient of $0.01 \text{ mV}\cdot\text{K}^{-1}$, close to the expected value of *ca.* $0 \text{ mV}\cdot\text{K}^{-1}$, (notably close to the thermoelectric Seebeck coefficient of copper, $+0.002 \text{ mV}\cdot\text{K}^{-1}$ [14]).

Table 1 - Temperature dependence of cell potentials of investigated systems

Electrodes	Temperature profile	$\Delta V/\Delta T$ / mV·K ⁻¹
Li Li	Stepped gradient	+0.98±0.03
	Pulsed gradient	+1.00±0.02
Li _{3.5} Fe(CN) ₆ Li _{3.5} Fe(CN) ₆	Pulsed gradient	-0.57±0.06
Li Li _{3.5} Fe(CN) ₆	Pulsed isothermal (both heated)	+4.3±0.4
	Pulsed gradient (Li _{3.5} Fe(CN) ₆ heated)	+3.9±0.5
	Pulsed gradient (Li heated)	+0.7±0.2

The same experiment was performed using a symmetrical cell with two identical composite Li_{3.5}Fe(CN)₆ intercalation electrodes. This experiment would reveal the temperature dependence of $\text{Li}_{(\text{intercalated})} \rightarrow \text{Li}^+_{(\text{solvated})} + \text{e}^-$. Given that the entropy change is dominated by (de)solvation of the lithium ion [5, 9], it was expected that a symmetrical cell would yield similar results to the lithium metal symmetrical cell, *cf.* already reported values between +0.6 mV·K⁻¹ to +1.2 mV·K⁻¹ for two lithium intercalation electrodes [9].

Attempts to measure this cell using stepped temperature gradients showed significant drift in potential over time; a similar drift appears in literature data [9, 10]. However, background-corrected pulsed temperature gradient measurements were found to yield stable results, without hysteresis, as shown in Figure 2c. Surprisingly, pulsed temperature gradient measurements of a symmetrical cell with Li_{3.5}Fe(CN)₆ electrodes gave a value of -0.57±0.06 mV·K⁻¹ (Table 1). The inverted sign indicates that the entropic direction of the cell is inverted; release of the intercalated Li⁺ moderately *increases* entropy in the system, despite solvation of this ion *reducing* local entropy.

A previous investigation of an asymmetric cell with one electrode being lithium metal and the other $\text{Li}_x\text{Co}[\text{Fe}(\text{CN})_6]_{0.9}$ was carried out only under pulsed isothermal conditions [10]. The assumption was that the $\text{Li}_{(s)} \rightarrow \text{Li}^+_{(\text{solvated})} + e^-$ is temperature independent, and that observed temperature differences between the two electrodes correspond to the Seebeck coefficient of the $\text{Li}_x\text{Co}[\text{Fe}(\text{CN})_6]_{0.9} \rightarrow \text{Li}^+_{(\text{solvated})} + \text{Li}_{x-1}\text{Co}[\text{Fe}(\text{CN})_6]_{0.9} + e^-$ process. Significant hysteresis was observed between heating and cooling cycles, and the degree of intercalation (x) was also significant. The largest and smallest Seebeck coefficients were *ca.* -0.76 and $+0.81 \text{ mV}\cdot\text{K}^{-1}$ ($x = 0.21$ and 0.96 , respectively); for all values of x greater than 1, the value was *ca.* $+1 \text{ mV}\cdot\text{K}^{-1}$.

As we have confirmed that the $\text{Li}_{(s)} \rightarrow \text{Li}^+_{(\text{solvated})} + e^-$ process corresponds to *ca.* $1.0 \text{ mV}\cdot\text{K}^{-1}$ (via measurements with the same electrolyte system as reported in [10]), this allows us to 'correct' the reported values from above to -1.76 and $-0.19 \text{ mV}\cdot\text{K}^{-1}$ ($x = 0.21$ and 0.96) for the $\text{Li}_x\text{Co}[\text{Fe}(\text{CN})_6]_{0.9} \rightarrow \text{Li}^+_{(\text{solvated})} + \text{Li}_{x-1}\text{Co}[\text{Fe}(\text{CN})_6]_{0.9}$ process. That these values have the same sign (negative) demonstrates a uniform entropic direction; release of intercalated Li^+ *increases* entropy in the system, in line with our own observations. The effect decreases as the intercalation material approaches saturation; when x is above 1, the Seebeck coefficient approaches $0 \text{ mV}\cdot\text{K}^{-1}$. However, it should also be noted that our results present issues when equating symmetric and asymmetric cells (see below).

On considering isothermal heating of an asymmetrical cell, with lithium metal as one electrode and the intercalation compound $\text{Li}_{3.5}[\text{Fe}(\text{CN})_6]$ as the other, the potential difference between the electrodes was expected to decrease by *ca.* $-1.6 \text{ mV}\cdot\text{K}^{-1}$. This is because our symmetrical cell results predict the two half-cell potentials will shift in different directions and ultimately approach each other. However, a value of $+4.3 \pm 0.4 \text{ mV}\cdot\text{K}^{-1}$ was

observed. This discrepancy indicates that the Seebeck coefficient of these asymmetric systems is not a simple temperature dependence of the electrode potential of the two half-cells.

To investigate these cells further, the two sides of the cell were subjected to pulsed temperature gradients, and the potential differences recorded. Heating the lithium intercalation electrode gave a Seebeck coefficient of $+3.9 \pm 0.5 \text{ mV} \cdot \text{K}^{-1}$. Conversely, on heating only the lithium metal electrode, the Seebeck coefficient dropped to $+0.7 \pm 0.2 \text{ mV} \cdot \text{K}^{-1}$. It is notable that (i) heating just the intercalation electrode gives the same value (within error) as isothermal heating of the whole cell, and (ii) the sum of the Seebeck coefficients from the two non-isothermal measurements ($4.5 \pm 0.5 \text{ mV} \cdot \text{K}^{-1}$) also results in the same value (within error) as isothermal heating of the whole cell. It is unclear which observation, if either, is the valid one.

For the asymmetric cells, a Seebeck coefficient of *ca.* $+4 \text{ mV} \cdot \text{K}^{-1}$ is consistent with the overall dissolution of $\text{Li}_{(\text{s})}$ and intercalation of Li^+ being the entropically favourable process. However, the magnitudes of the observed results are not consistent with this simple model, nor with the idealised half-cells of $\text{Li}_{(\text{s})} \rightarrow \text{Li}^+_{(\text{solvated})} + \text{e}^-$ and $\text{Li}^+_{(\text{solvated})} + \text{e}^- \rightarrow \text{Li}_{(\text{intercalated})}$. Two possible explanations are that (i) intercalation of the solvent or interaction of the solvent with the surface of the intercalation material is strongly affected by the degree of intercalation of Li^+ , and (ii) the two processes are not symmetrical, with the (de)solvation for each proceeding through different entropic pathways.

Regarding point (i), there is little evidence of solvents such as DEC and EC being co-intercalated [15] (with the exception of graphite [16]). However, ‘thermocapacitive’ effects are known, where the temperature-dependent nature of the double layer is instrumental in generating significant Seebeck coefficients between -0.918 and $+2.413 \text{ mV}\cdot\text{K}^{-1}$ [17, 18]. Notable changes in the surface charge could occur at the intercalation material's surface, resulting in the observed changes. For example, desolvation of a single ion could be offset by larger structural changes in the double layer, possibly accounting for the inversion of the Seebeck coefficient for intercalation materials, relative to the metal. Activity coefficients for $\text{Li}^+_{(\text{intercalated})}$ would not be expected to vary significantly across most of the intercalation values, yet the Seebeck coefficient is significantly affected by the degree of lithium intercalation [9, 10]; a thermocapacitive effect could explain these observations. Additionally, the intercalation electrode contained carbon black which could have a thermocapacitive effect of its own [17].

Regarding point (ii), the electrodeposition/electrodissolution and intercalation/release of lithium could correspond to significantly different reaction pathways. If different kinetic and thermodynamic reaction pathways occur at the two electrodes, the rate-limiting “ $\text{Li}^+_{(\text{solvated})}$ ” might not be the same at each electrode. While this cannot explain the inversion in the sign of the Seebeck coefficient, it could explain the more complicated results on combining dissimilar half-cells.

5 Conclusions

The temperature dependence of lithium metal electrodes and lithium intercalation electrodes were observed to be significantly different, even with opposite signs. This is attributed to different entropic pathways; likely a consequence of different (de)solvation pathways *and* different interactions between the solvent and the intercalation material (as a function of intercalation). When a lithium metal electrode and a lithium intercalation electrode were combined in an asymmetric cell (*cf.* a battery arrangement), even more significant differences were observed, suggesting a 'synergy' not predicted by their individual half-cell measurements. This is very significant for safer battery design, where temperature gradients across cells and temperature differences between cells in a stack are relevant to battery longevity and safety; subsequent confirmation and quantification of the fundamental thermodynamic (presumably primarily entropic) driving forces responsible are encouraged.

Conflicts of Interest

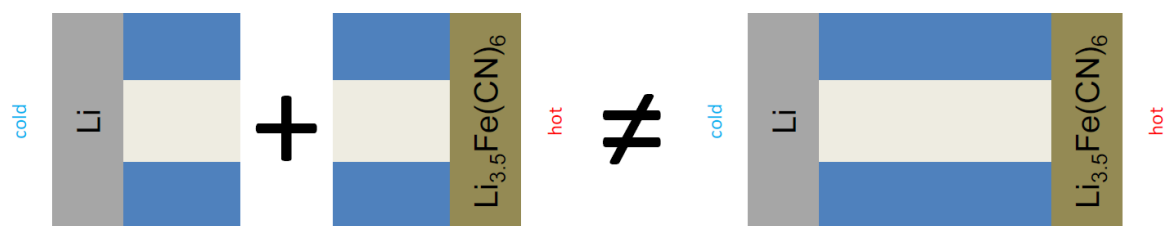
There are no conflicts of interest.

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Graphical abstract

Highlights

- Lithium has a significant thermogalvanic Seebeck coefficient (*ca.* 1 mV K⁻¹)
- Asymmetric assemblies are not governed by their thermal half cells
- Asymmetric cells can't reliably be used to measure Seebeck coefficient of half-cells
- Asymmetric lithium ion battery assemblies display synergy in response to thermal gradients